Ferrofluids are new class of magnetic materials, which combine both fluidic and magnetic properties. This rare combination leads to various unusual fundamental phenomena as well as numerous interesting applications. Magnetic fluids can be confined, positioned, shaped and controlled by an external magnetic field of moderate strength and hence becomes a challenging subject for those doing fundamental research leading to a wide range of application. Rapid progress has been made in the past thirty-five years in the production of magnetic fluids for various technological applications.

Magnetically responsive fluid (ferrofluids) consists of magnetic nano-particles (30 to 100 Å) coated with a suitable surfactant and colloidally dispersed in a non-magnetic carrier liquid. Magnetic fluid research has taken a serious transition presently, taking into account the non-potential bulk forces in magnetically non-uniform fluids, and opens promising design of new applications particularly intensification of the heat transfer for cooling the high power electric transformers. Ferrofluids can be effectively used as heat carriers.

For different technological applications, one has to synthesize ferrofluids with varying physical properties. Thermomagnetic energy conversion using ferrofluids proposed during the early stage of research has not yet been fully realized. In order to use ferrofluids for thermal dissipation, it is necessary to use a fluid with large pyromagnetic coefficient, i.e., fluid with a high saturation magnetization and a low Curie temperature. Magnetically induced convection is generated by the inhomogeneity of magnetic fluid volume force developed in a non-uniform magnetic field. Mn-Zn ferrite nano-particles are used for the preparation of temperature sensitive ferrofluids. However, the magnetic fluid (having Mn-Zn ferrite particles) considered for the above application has a low magnetic volume force due to comparatively low magnetization of particles. Hence in order to prepare ferrofluids for thermomagnetic energy conversion and to make use of the magnetically induced convection for thermal dissipation Co-Zn ferrite nano-particles could be effectively used.
Preface

Preparation and properties of Co-Zn ferrite nano-particles and ferrofluids having Co-Zn ferrite particles have not yet been studied exclusively like Mn-Zn ferrites. In the light of these, Co-Zn and Mn-Zn substituted ferrite nano-particles, which can be used for ferrofluids preparation, have been synthesized and characterized. The effect of zinc substitution on the physical properties of the fine particles and ferrofluids are also studied.

The aim of the thesis is to synthesize and study the properties of Mn-Zn and Co-Zn substituted ferrite nano-particles used in the preparation of ferrofluids. Among different magnetic materials zinc substituted spinel ferrites are attractive because Zn$^{2+}$ substitution alters their magnetic parameters in a wide range of values. Ferrofluids having $\text{Me}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ fine particles ($\text{Me} = \text{Mn}^{2+}, \text{Co}^{2+}$) with $x$ varying from 0.1 to 0.5 were prepared by the usual chemical co-precipitation method.

The thesis entitled “The effect of zinc substitution on Mn-Zn and Co-Zn ferrite nano-particles used in the preparation of ferrofluids” consists of six chapters and the contents of each chapter are as follows:

The first chapter provides a review of the important developments in both preparation and application aspects of ferrofluids. It includes a brief introduction to ferrofluids, preparation aspects, size restriction imposed by the stability requirements, magnetic materials used and their magnetic properties. Purpose and task of the thesis with justification for the samples chosen and ferrofluids for heat dissipation using the magnetically induced convection are also discussed.

Second chapter describes the experimental techniques used in the characterization of fine particles and ferrofluids. The following experimental techniques have been used. X-ray diffraction was used for structural analysis and determination of crystallite size. Indexing and refining of cell parameters were carried out by using “Powder-X” software. The average crystallite size for each composition was calculated using the Debye-Scherrer formula.
The full widths at half the maximal value were obtained for the indexed peaks after deconvoluting, using peak-fit software. The size, shape and morphology of the particles were also observed using high-resolution transmission electron microscopy. The percentages of Mn$^{2+}$, Co$^{2+}$ and Zn$^{2+}$ in the final product were determined using the spectrophotometry technique. The Fe$^{3+}$ ions were determined colorimetrically. SEM with EDAX was used for the elemental analysis of the particles after grinding. The associated water content was determined by thermogravimetric analysis, i.e. monitoring the weight of the sample while it is heated slowly, in our case up to 973 K, in an inert atmosphere.

Magnetization measurements of the powder samples were made at room temperature up to a field of 796 kA/m and the temperature dependence of magnetization was measured by varying the temperature in a field of 398 kA/m using a Vibrating Sample Magnetometer. The temperature dependence of magnetization of the powder samples was also recorded in a field of 80 kA/m using a pulse field technique. Magnetization of the fluid samples was measured in fields up to 80 kA/m using pulse field technique and the saturation magnetization of the fluid samples was obtained by fitting with theoretical equation.

The third chapter deals with the synthesis and characterization of Mn-Zn and Co-Zn ferrite nano-particles. Ultra fine particles of $\text{Me}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($\text{Me}^{2+}$ Mn$^{2+}$ or Co$^{2+}$) with $x$ varying from 0.1 to 0.5 were prepared by adding an excess of alkali to aqueous solutions of divalent and trivalent metal ions. The reaction mixtures were maintained at 368 K for one hour. This duration was sufficient for the transformation of hydroxides into spinel ferrite.

The results obtained from the X-ray analysis, TEM, TGDTA, AAS and spectrophotometry are also discussed. The X-ray diffraction pattern indicates the formation of Mn-Zn and Co-Zn ferrite nano-particles. The average crystallite size calculated using the Debye-Scherrer formula was found to decrease with increasing zinc concentration.
The percentage of zinc in the particles affects the adsorbed water content. The adsorbed water content increases from 3.75 % to 15.10 % in the case of Mn-Zn ferrite and from 11.0 % to 16.7 % in the case of Co-Zn ferrite, with the increase in zinc concentration. The composition of the ferrites was in accordance with the relative concentrations of the metals in the reaction mixture. The ratio of \[\frac{[\text{Me}^{2+}] + [\text{Fe}^{3+}]}{[\text{Zn}^{2+}] + [\text{Co}^{2+}]}\] initially taken was 0.5. The ratio in the final product varied from 0.512 to 0.520 in the case of Co-Zn ferrite and from 0.50 to 0.51 in the case of Mn-Zn ferrites.

Chapter four discusses the magnetic properties of the fine particles. The room temperature magnetization and the temperature dependence of magnetization of the powder samples were determined and discussed. The Curie temperature of the prepared samples was determined by extrapolating the linear section of the temperature dependent magnetization curve to the temperature axis. The temperature dependence of magnetization showed a clear non-linear tail a phenomenon called 'paraprocess'.

Thermomagnetic coefficient \(k_1\) \((k_1 = -\Delta M/\Delta T)\) is the first derivative of the temperature dependent magnetization curve. The value of \(k_1\) was \(\geq 0.2\) only when \(0.5 \geq x \geq 0.2\) for both Mn-Zn and Co-Zn ferrite fine particles. The magnetic parameters like specific magnetization \(M_s\), remanence \(M_r\) and coercivity \(H_c\) of the prepared fine particles measured at room temperature in a maximum field of 796 kA/m (10 kOe) showed a strong dependence on the zinc concentration. The change in magnetic properties such as \(M_s\), \(H_c\) and Curie temperature \(T_C\) is due to the influence of the cationic stoichiometry and their occupancy of the specific sites.

The specific magnetization of the Co-Zn substituted ferrite nano-particles decreases continuously with increasing zinc concentration whereas the specific magnetization of Mn-Zn substituted ferrite nano-particles showed a maximum for \(x = 0.2\) and decreases upon further increase in zinc concentration.
Room temperature Mössbauer spectra for the representative samples (x=0.1, 0.3 and 0.5) were recorded for both Mn-Zn and Co-Zn ferrite nano-particles. The fine particles with high zinc concentration whose particle size are less than or equal to 10 nm, show only a quadrupole doublet. But the particles with particle size greater than 10 nm (for x=0.1) exhibit complex hyperfine structure. The Mössbauer study also shows that the particle size decreases with increase in the zinc concentration.

The preparation and properties of ferrofluids having Mn-Zn and Co-Zn fine particles are given in chapter five. The procedure for preparing ferrofluids having low viscosity based on volatile hydrocarbons is discussed. Oleic acid was used as the surfactant and coating of surfactant was carried out at a temperature of about 353 K (80°C). To coagulate the oleic acid coated particles, dilute HNO₃ was added. After decantation, the coated particles were dispersed in heptane and centrifuged. Mn₀.₃Zn₀.₇Fe₂O₄ and Co₀.₃Zn₀.₇Fe₂O₄ fine particles were used for the preparation of temperature sensitive ferrofluids. Subsequently, the preparation of temperature sensitive ferrofluid, using the fine particles with selected value of the thermomagnetic coefficient is given in this chapter.

The results obtained from the magnetization measurements of the fluid samples carried out by pulse field technique to a maximum field of 80 kA/m at room temperature are discussed. Temperature sensitive ferrofluids based on Mn₀.₃Zn₀.₇Fe₂O₄ and Co₀.₃Zn₀.₇Fe₂O₄ particles with high value of the thermomagnetic coefficient can be used for thermal dissipation. Ferrofluids having Co₀.₃Zn₀.₇Fe₂O₄ particles shows a high value of magnetization and will consequently have a high magnetic volume force in comparison with fluids having Mn₀.₃Zn₀.₇Fe₂O₄ particles.

Sixth chapter constitutes the salient features of the experimental results together with the summary and conclusion.